SPECIFIC EXTINCTION COEFFICIENT OF FLAME GENERATED SMOKE

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Reprinted from the Fire and Materials, Vol. 24, No. 5, 227-230, September/October 2000.

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NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

FIRE AND MATERIALS
Fire Mater. **24,** 227–230 (2000)

Specific Extinction Coefficient of Flame Generated Smoke†

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The experimental results for the mass specific extinction coefficient (σ_s) at $\lambda = 633$ nm for flame generated smoke are summarized for seven studies involving 29 fuels. The measurements are for post-flame smoke generated by overventilated burning. From an analysis of variance for the seven studies, it was found that between-laboratory differences were the major source of variability. The estimated mean value of σ_s is 8.7 m^2/g with an expanded uncertainty (95% confidence interval) of 1.1 m^2/g. A major implication of this nearly universal value is that one can infer mass concentration of smoke by making light extinction measurements. Published in 2000 by John Wiley & Sons Ltd.

INTRODUCTION

The mass specific extinction coefficient of smoke, σ_s, is needed for determining the mass concentration of post-flame smoke via light extinction measurements. If the value of σ_s were known, then light extinction measurements could be used for determining the smoke yield for fuels/materials found in constructed facilities using furniture and cone calorimeters.[1] Such a measurement of smoke concentration could also be used for validation of field and zone computational models for smoke flow and dispersion in building and oil spill fires.

Bouguer's Law as applied to smoke is the basis for relating optical measurement and mass concentration. Specifically, Bouguer's Law relates the ratio of the transmitted and incident intensities to the mass concentration of smoke M_s (mass/volume), the pathlength through the smoke, L, and σ_s via the following expression

$$\frac{I}{I_0} = exp(-\sigma_s M_s L). \quad (1)$$

The general utility of this approach is based on the hypothesis that σ_s is nearly universal for post-flame smoke produced from overventilated fires. The basic qualitative ideas that support this hypothesis are that soot from all flames is primarily carbon with a primary sphere size much smaller than the wavelength of light and a fractal dimension less than two. For these conditions, the light absorption cross section is proportional to the mass and is the dominant contribution to the light extinction coefficient. There will be a smaller contribution from the light scattering cross section which depends on the agglomerate size.

In this brief paper, the experimental results for σ_s measured for post-flame smoke in seven studies will be summarized. From a statistical analysis of these results, a mean value will be obtained along with the uncertainty in the mean. This analysis will provide the basis for making quantitative smoke concentration measurements via light extinction measurements. Currently this is only possible by filter collection and gravimetric measurements.

REVIEW OF EXPERIMENTAL STUDIES OF σ_s

A brief discussion of the salient features of seven measurements of σ_s is presented. The results are presented for measurements made at a wavelength of 633 nm, which corresponds to a HeNe laser beam. Only two of the studies included a quantitative uncertainty assessment.

The study by Newman and Steciak[2] includes eight different solid and liquid fuels found in buildings, homes and urban areas. Measurements were made for both small and large scale samples though there was no discussion of scale effect. The values of σ_s were not given in the paper. We determined these values by dividing the ratio of extinction coefficient to particle volume fraction given in Table 2 of their paper by their measured density of the smoke particulate, 1.1 g/cm^3. The average for the eight samples is 10.2 m^2/g with a standard deviation of 0.20 m^2/g, which is the smallest standard deviation of the seven studies. The low value of the standard deviation is, in part, a result of using an average density for the smoke. If individual tests were analysed in terms of the light extinction coefficient and the mass concentration of smoke, it is expected that a larger variability would have been obtained.

Measurements were carried out by Mulholland *et al.*[1] and by Dobbins *et al.*[3] on fire sizes ranging from 50 kW to 350 kW to determine the effects of scale and material chemistry on the smoke yield and σ_s. The fuels included construction wood, rigid polyurethane and three hydrocarbons. The first of these studies[1] reported the only large scale tests with repeatability data. For each fuel, eight to ten repeat measurements were made with a typical standard

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† This article is a U.S. Government work and is in the public domain in the U.S.A.

Published in 2000 by John Wiley & Sons, Ltd.
Received 27 December 1999
Accepted 10 July 2000

deviation of 1.0 m^2/g. The average value of σ_s was 8.2 m^2/g with a standard deviation of the five fuel averages of 0.40 m^2/g, which is the next to the smallest value.

The study by Patterson *et al.*[4,5] at Georgia Tech involved the widest range of materials, which were burned at a scale slightly smaller than a typical 10 cm × 10 cm cone calorimeter sample. In determining the average value for each fuel, only the tests involving flaming combusion without evidence of smouldering or pyrolysis were included. The average value for the eleven fuels was 8.5 with a standard deviation of 1.01, which is the largest of the seven studies. The larger standard deviation for the averages compared with the large scale test above is, in part, a result of the shorter optical pathlength and the flow uncertainty for the varying stack temperature.

Choi *et al.*[6] carried out measurements under premixed conditions. This is the first study to make a quantitative uncertainty estimate resulting in an expanded uncertainty of 1.1 m^2/g (95% confidence level) about an average value of 7.8 m^2/g for the burning of acetylene. The stack temperature for these experiments was about 500 K, and there was a significant radial variation in temperature and smoke concentration.

Colbeck *et al.*[7] measured σ_s for small scale liquid and gaseous hydrocarbons flames and obtained the largest average value of 10.4 and the second largest standard deviation with a value of 1.00 m^2/g. The measurement uncertainty was not discussed in this paper.

Mulholland and Choi[8] reduced the measurement uncertainty of σ_s by a factor of two to three from previous studies by making the following design changes: longer optical pathlengths, reduced drift in the light intensity, steady state smoke source, and accurate flow calibrations. An absolute calibration of the system was performed using monosize polystyrene spheres with known size, density and refractive index. The mean value of 8.78 m^2/g is close to the average for all the studies and the value of σ_s obtained for the diffusion burning of acetylene was very close to the premixed result.

Wu *et al.*[9] and Krishnan *et al.*[10] used similar facilities at the University of Michigan to measure σ_s for gaseous and liquid hydrocarbons. Only the values obtained from the more recent study, which are about 50% larger than the earlier study, are reported here. Still the average value of σ_s obtained in this study, 7.0 m^2/g, is lower than the next closest value by 15%. The results from these studies are reported as dimensionless extinction coefficients. The conversion factor from mass specific extinction to dimensionless extinction is equal to the product of the particle density and the wavelength of the HeNe laser. An average soot density of 1.9 g/cm^3 is used based on the densities reported by Wu *et al.*[8] The values given in Table 1 are estimated from the graph in Fig. 8.[10]

UNCERTAINTY ASSESSMENT

The values of σ_s from seven studies are given in Table 1 along with the average and standard deviation for each study. The results are also displayed graphically as σ_s vs fuel with the laboratories identified numerically. It is apparent from Fig. 1 that the values for each laboratory are clustered while the laboratory to laboratory variations are greater. An analysis of variance shows a significant between-laboratory effect, meaning that there are systematic differences among the laboratories. This between-laboratory effect is the dominant source of variability.

It is reasonable to assume that results from individual laboratories are independent, one from another, and, therefore, the best estimate of a universal value for the extinction coefficient given the lack of uncertainty analysis by five of the seven laboratories is the average of laboratory averages. This value is 8.71 m^2/g, and the standard deviation of the seven values is $s = 1.23$ m^2/g with six degrees of freedom. It is reassuring that the study[8] with the lowest measurement uncertainty obtained a mean value of 8.78 m^2/g in good agreement with the value of 8.71 m^2/g.

The standard deviation of the laboratory average, s_{avg}, is obtained by dividing s by the square root of the number of values.

$$s_{avg} = \frac{s}{\sqrt{7}}$$

The resulting value is $s_{avg} = 0.465$ m^2/g.

The expanded uncertainty for the universal value is

$$U = k s_{avg}$$

where k is a coverage factor from Student's t distribution. For approximate 95% coverage, $k = 2.447$, and

$$U = 1.14 \text{ m}^2/\text{g}.$$

It is of interest to also estimate the effect of the fuel chemistry, the effect of fire scale/burner type, and the effect of the agglomerate size on σ_s. To obtain an estimate of the chemistry effect we pool the standard deviations form studies involving three or more fuels and obtain a value of 0.83 m^2/g. We omit the Newman and Steciak study[2] because of the unrealistic small effect of fuel chemistry as discussed above. This value of 0.83 m^2/g may be somewhat inflated because it includes within-laboratory measurement uncertainty. In the study by Mulholland and Choi,[8] the measurement uncertainty was reduced so that the chemistry effect could be measured. The standard deviation of σ_s for three fuels, chosen to show the maximum fuel effect, is 0.95 m^2/g. The individual values are within the expanded uncertainty limits as shown in Fig. 1.

The second factor is the effect of fire scale/burner type. Unpublished data obtained at NIST in 1988 by the same method as described by Mulholland *et al.*[1] include results for a range of fire sizes for each of five fuels typically involving three repeat tests at a fire size of about 80 kW and at about 250 kW. The standard deviations based on the averages for the two fire sizes for the five fuels range from a minimum of 0.14 m^2/g to a maximum of 0.64 m^2/g with a mean value of 0.49 m^2/g.

There is a lack of quantitative data on the effect of burner configuration for the larger scale fires. There is an extensive data base for ethene and acetylene using both laminar burner and a small turbulent burner. The standard uncertainty associated with the burner effect is 0.2 m^2/g.

The third factor is the effect of agglomeration. This was assessed by collecting smoke from burning of crude oil in

Table 1. Summary of mass specific extinction coefficients at $\lambda = 632.8$ nm for seven studies

Lab #[a]/Ref.	Fuel, #[b]	Scale	Avg. σ_s (m^2/g)	SD[c] (m^2/g)	U[d] (m^2/g)
1/2	Heptane, 1	Small to large	10.3		
1/2	Kerosene, 2		10.1		
1/2	Douglas fir, 3[e]		10.3		
1/2	PMMA[f], 4		10.5		
1/2	PVC[f], 5		9.9		
1/2	PC[f], 6		10.2		
1/2	PS[f], 7		10.0		
1/2	Styrene-butadiene rubber, 8		10.4		
Laboratory #1, avg. $\pm$ SD[g]		10.2 $m^3/g \pm 0.20$ m^2/g			
2/1,3	Propane, 9	170 kW to 350 kW	8.0	1.1	
2/1,3	Heptane, 1	30 cm (60 kW) and 50 cm pools (250 kW)	7.8	0.9	
2/1,3	Wood crib[h], 3	1 crib (50 kW) 3 cribs (250 kW)	8.5	1.0	
2/1,3	Polyurethane crib, 10	1 crib (100 kW) 3 cribs (300 kW)	8.1	1.1	
2/1,3	Crude oil, 11	40 cm (60 kW) and 60 cm (180 kW) pools	8.8	0.9	
Laboratory #2, avg. $\pm$ SD		8.2 $m^2/g \pm 0.40$ m^2/g			
3/5	PMMA, 4	Small scale, 1 kW to 5 kW	7.9	2.4	
3/5	PC, 6	Small scale, 1 kW to 5 kW	7.6	1.0	
3/5	PVC, 5	Small scale, 1 kW to 5 kW	9.0	0.9	
3/5	HDPE[f], 12	Small scale, 1 kW to 5 kW	8.8	2.5	
3/5	PS, 7	Small scale, 1 kW to 5 kW	9.6		
3/5	PP[f], 13	Small scale, 1 kW to 5 kW	7.4		
3/5	Oak, 3	Small scale, 1 kW to 5 kW	7.6	2.4	
3/5	Rubber, 14	Small scale, 1 kW to 5 kW	10.1		
3/5	Kerosene, 2	Small scale, 1 kW to 5 kW	9.2		
3/5	Fuel oil #2, 15	Small scale, 1 kW to 5 kW	7.2	1.7	
3/5	Fuel oil #5, 16	Small scale, 1 kW to 5 kW	9.4	0.6	
Laboratory #3, avg. $\pm$ SD		8.5 $m^2/g \pm 1.01$ m^2/g			
4/6	Acetylene, 17	Premixed burner at equivalence ratio of 2.5	7.8	0.4	1.1
Laboratory #4, avg.		7.8 m^2/g			
5/7	Petrol, 18	5 ml of fuel	11.2		
5/7	Diesel, 19	5 ml of fuel	10.3		
5/7	Fuel oil, 20	5 ml of fuel	11.6		
5/7	Paraffin oil, 21	5 ml of fuel	9.1		
5/7	Butane, 22	5 ml of fuel	9.9		
Laboratory #5, avg. $\pm$ SD		10.4 $m^2/g \pm 1.00$ m^2/g			
6/8	Acetylene, 17	5 cm dia. burner, 2.6 kW	7.80	0.08	0.43
6/8	Ethene, 23	5 cm dia. burner, 2.0 kW	8.79	0.28	0.65
6/8	Styrene, 24	2 cm diameter pool	9.7	0.35	0.90
Laboratory #6, avg. $\pm$ SD		8.78 $m^2/g \pm 0.95$ m^2/g			
7/10	Acetylene, 17	Turbulent diffusion burner, 5 kW to 10 kW	5.3		
7/10	Ethene, 23	Turbulent diffusion burner, 5 kW to 10 kW	7.8		
7/10	Propylene, 25	Turbulent diffusion burner, 5 kW to 10 kW	7.0		
7/10	Butadiene, 26	Turbulent diffusion burner, 5 kW to 10 kW	7.5		
7/10	Benzene, 27	Turbulent diffusion burner, 5 kW to 10 kW	7.8		
7/10	Cyclohexane, 28	Turbulent diffusion burner, 5 kW to 10 kW	7.5		
7/10	Toluene, 29	Turbulent diffusion burner, 5 kW to 10 kW	7.0		
7/10	heptane, 1	Turbulent diffusion burner, 5 kW to 10 kW	6.4		
Laboratory #7, avg. $\pm$ SD		7.0 $m^2/g \pm 0.85$ m^2/g			

[a] 1, Factory Mutual; 2, NIST Large Scale Fire Research Laboratory; 3, Georgia Tech Combustion Characterization Facility; 4, NIST Fire Science Division Laboratory; 5, University of Essex Institute for Environmental Science; 6, NIST Large Agglomerate Optics Facility; 7, University of Michigan Buoyant Turbulent Flame Facility.

[b] # refers to the fuels plotted in Fig. 1.

[c] SD refers to the standard deviation for repeat measurments of the same fuel.

[d] U refers to the expanded uncertainty (95% confidence interval).

[e] Douglas fir, wood cribs and oak are all considered the same fuel.

[f] Abbreviations for polymers: PMMA, polymethylmethacrylate; PVC, polyvinylchloride; PC, polycarbonate; PS, polystyrene; HDPE, high density polyethylene; PP, polypropylene.

[g] Laboratory average and standard deviation for all the fuels measured.

[h] Crib refers to an ordered array of wooden sticks.

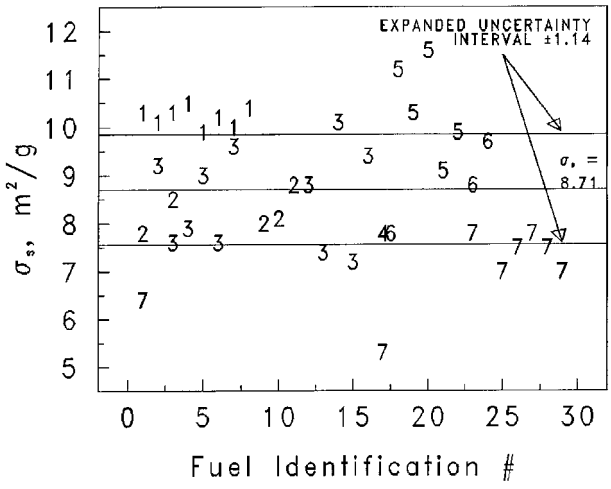

Figure 1. Scatter plot of the specific extinction coefficient versus fuel for seven studies of postflame smoke. The correspondence between number and fuel is given in Table 1.

a 1 m^3 chamber and measuring the specific extinction as a function of time over a period of about 1 h.[3] During this time, the average cluster size grew from about 200 primary spheres to about 4000, and the change in σ_s was about 0.33 m^2/g.

DISCUSSION

The observed effects of fire scale/burner size and agglomerate size on σ_s are small compared with the effect of the fuel chemistry. Still, the between-laboratory effect is the major source of uncertainty and is the basis of the uncertainty estimate. In one study,[8] the chemistry effect exceeded the measurement uncertainty. If future studies are carried out with an uncertainty comparable to that study, it would be expected that the between-laboratory uncertainty would decrease and the fuel chemistry would be the major component of the uncertainty.

The recommended value of the mass specific extinction coefficient of post-flame generated smoke is 8.7 m^2/g with an expanded (95% confidence interval) uncertainty of 1.1 m^2/g. This value applies to overventilated flaming combustion such as burning in an open area.

The value is smaller and more variable for smoulder or pyrolysis generated smoke with a mean value of about 4 m^2/g to 5 m^2/g.[5,11] The smaller value is a result of the low light absorption of this smoke. The variability in the coefficient results from the sensitivity of light extinction to the range in smoke droplet size from about 0.1 μm to about 3 μm. For this smoke, light scattering is the major contributor to the light extinction. For flame generated smoke, light absorption is the dominant contributor to the light extinction and the light absorption cross section per mass is relatively insensitive to primary particle size, since even the largest is at least a factor of 10 smaller than the HeNe laser wavelength of 633 nm.

The value of σ_s may be smaller for underventilated combustion such as burning in an enclosure where the pyrolysis rate of the fuel exceeds the inflow rate of air required for its stoichiometric burning. The value of σ_s was measured for smoke produced by underventilated laminar combustion of ethene with an equivalence ratio of 3 (1/3 the amount of air needed for stoichiometric burning) and a value of about 7 m^2/g was obtained using the large agglomerate optics facility described by Mulholland and Choi.[8] This value is 18% lower than the value of 8.5 m^2/g obtained for overventilated laminar combustion of ethene.[8]

This universal value also depends on the smoke being produced being primarily carbonaceous soot. This is a good approximation for the burning of CH and CHO fuels. The results in Table 1 for PVC and polyurethane[2,5] indicate that the value is also valid for at least some chlorine and nitrogen containing fuels. On the other hand, for fuels with high Si content such as dimethylsiloxane, the value of σ_s is much lower as a result of the production of silica.[12]

One application of this universal value of σ_s is the measurement of the mass generation rate of smoke using light extinction measurements. Mulholland *et al.*[13] have demonstrated the feasibility of making quantitative measurements of smoke yield and smoke production rate using this approach.

REFERENCES

1. Mulholland GW, Henzel V, Babrauskas V. *Proceedings of the 2nd International Symposium on Fire Safety Science*, 1989; 347.
2. Newman JS, Steciak J. *Comb Flame* 1987; **67**: 55.
3. Dobbins RA, Mulholland GW, Bryner NP. *Atm Environ* 1994; **28**: 889.
4. Patterson EM, Duckworth RM, Wyman CM, Powell EA, Gooch JW, *Atm Envi* 1991; **25**: 2539.
5. Patterson EM, Duckworth RM, Powell EA, Gooch JW. *Measurements of the Emissions Properties of Burning Plastic Material for Nuclear Winter Studies*, DNA-TR-90-98, Defense Nuclear Agency: Alexandria, VA (1991).
6. Choi MY, Mulholland GW, Hamins A, Kashiwagi T. *Comb Flame* 1995; **102**: 161.
7. Colbeck I, Atkinson B, Johar Y. *J Aero Sci* 1997; **28**: 715.
8. Mulholland GW, Choi MY. 27*th Symposium* (*International*) *on Combustion.* The Combustion Institute: Pittsburg, 1998; 1515.
9. Wu JS, Krishnan SS, Faeth GM. *J. Heat Transfer* 1997; **119**: 230.
10. Krishnan SS, Farias TL, Wu JS, Köylü ÜÖ, Faeth GM. *Mixing and Radiation Properties of Buoyant Luminous Flame Environments*: *II. Structure and Optical Properties of Soot.* Final Report to NIST for Grant 60NANB4D1696.
11. Seader JD, Einhorn. 16*th Symposium* (*International*) *on Combustion.* The Combustion Institute: Pittsburg. 1977; 1423.
12. Sivathanu Y, Hamins A, Mulholland GW, Kashiwagi T, Buch R. 7*th AIAA*/*ASME Joint Thermophysics and Heat Transfer Conference,* Vol. 1. 1998; 191.
13. Mulholland GW, Johnsson EL, Fernandez MG, Shear DA. to be published in *Fire and Materials.*